Intramolecular Rotation and the Structure of High Polymers. I. The Structure of Polypeptide Chain.

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I. Potential Curve of Internal Rotation. The results of experiments of Raman effect, infra-red absorption, dipole moment and electron diffraction made for ethylene dihalides by Mizushima, Morino, Watanabe, Simanouti, and others[1] in our laboratory have shown that there are three potential minima in one complete rotation about a carbon single bond as axis (see Fig. 1).

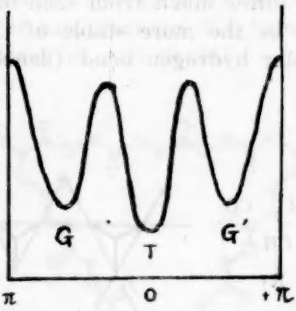

Fig. 1. Potential curve of ethylene dihalide.

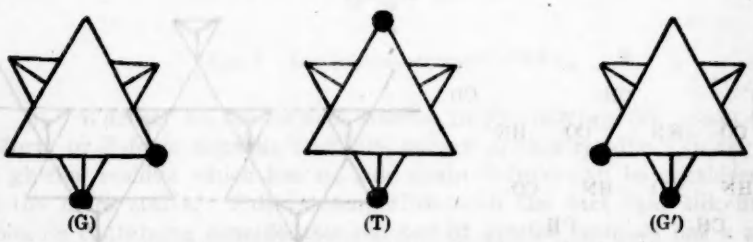

Fig. 2. Molecular forms corresponding to the three potential minima.

These three potential minima correspond to one trans form (T) in which two halogen atoms are at the farthest distance apart and two gauche forms (G and G') obtainable from the trans form by internal rotation

(1) Mizushima, Morino, and others: *Physik. Z.*, 35 (1934), 905; 38 (1937), 459; *J. Chem. Phys.*, 9 (1941), 826; Mizushima, Morino, Watanabe, Simanouti, and others; *Sci. Pap. I.P.C.R.* (Tokyo), 39 (1942), 396, 401; 40 (1942), 87, 100, 417, 425; 42 (1944), *Chem.*, 1, 5, 27, 51.

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of ±120° (see Fig. 2). The energy difference between the trans and the gauche minima amounts to 1 kcal/mol (1.2 kcal for ethylene dichloride and 1.3 kcal for ethylene dibromide). The height of potential barrier lying between these two kinds of minima amounts to about 10 kcal/mol, which is much smaller than the activation energy of ordinary chemical reactions so that "rotational isomers" of ethylene dihalides cannot be isolated under ordinary conditions. The experimental results obtained in our laboratory for ethylene chlorhydrin, chloral hydrate, normal paraffins,[2] and cyclohexane can also be explained by considering intramolecular potential of similar type.

II. The Basic Structure of Polypeptide Chain. As a stable configuration of polypeptide chain an extended form (Fig. 3) has already been proposed[3] which corresponds to the structure of silk fibroin or of β-keratin. However, from our experimental results stated in I we can propose another stable chain configuration (bent form) shown in Fig. 4. These two forms do not differ much from each other in internal energy and the bent form may be the more stable of the two because of the existence of intramolecular hydrogen bond (denoted by the dotted lines in Fig. 4).

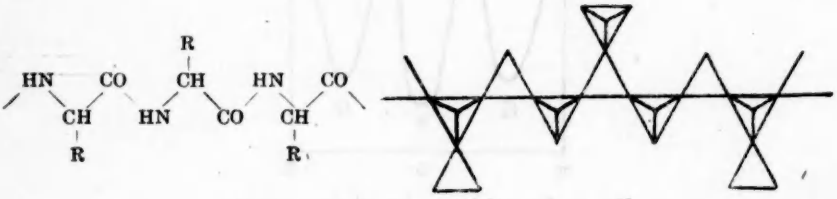

Fig. 3. Extended form.

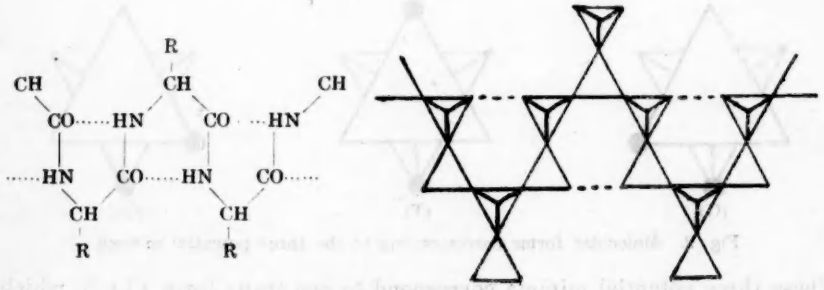

Fig. 4. Bent from.

Other stable forms are obtained by the suitable combination of these two basic structurs. Let us denote the unit structures of the extended

(2) Mizushima and Simanouti: *Proc. Imp. Acad. Tokyo,* 20 (1944), 86. The other results will be published before long.

(3) Meyer-Mark: *Hochpolymere Chemie* II, (1940).

and the bent forms by E and B respectively and hence represent the chain form of Fig. 3 by EEE ---- and that of Fig. 4 by BBB -----. Other conceivable structures are then denoted by EBEB ----, EEBEEB ----, EEEBEEEB ----, etc., among which the ring structures $(EB)_3$, $(EEEB)_3$, $(EBBB)_3$, etc. characterized by trigonal symmetry are included. Let us try to explain the experimental data obtained for proteins by these structures.

1) From the bond radii the period along the chain is calculated as 5.1 A for BBB---- and as 10.2 A for BBEBBE----. The experiment of Astbury made for keratin can be explained by these predicted values.[4] The mechanical properties of keratin fiber can also be accounted for by these structures as shown in next section.

2) The X-ray investigations show that the crystal structure of insulin,[5] excelsin,[6] etc. has trigonal symmetry. This is readily understood, if we consider that the molecule of such proteins is made of the said ring such as $(EEE ---- B)_3$, or by the suitable superposition of these plane forms. (The superposition may be caused through the hydrogen bond or the covalency of side chain).

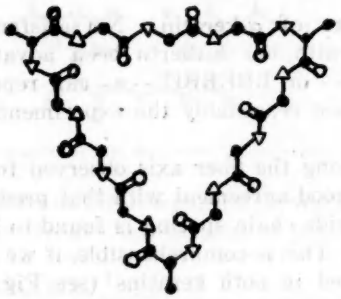

Fig. 5. The trigonal structure $(EEEB)_3$.

3) Whether an amino acid residue in the polypepetide chain takes E-form or B-form depends upon the nature of this residue. In the case of glycine residue which has no side chain E-form can be considered to be the more stable. This is compatible with the fact that silk fibroin molecule containing considerable number of glycine residues has a structure of β-keratin type or EEEEE ----.

In the case of a residue with the side chain which exerts large steric effect to the main chain or which strengthen the intramolecular hydrogen bond (denoted by the dotted line of Fig. 4), B-form becomes the more stable.

4) In any case these two forms E and B do not differ much in

(4) Astbury and Street: *Phil. Trans. Roy. Soc.* (London), A 230 (1931), 75.
(5) Crowfoot: *Proc. Roy. Soc.* (London), A 164 (1938), 580.
(6) Astbury, Dickinson, and Baily: *Biochem. J.*, 24 (1935), 2351.

their energy and the polypeptide chain tends to change its configuration by a slight change in the external condition. We can thus understand why some proteins are denatured easily and also why some proteins such as antibodies show quite specific properties.

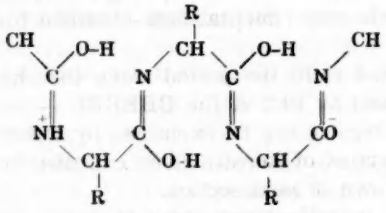

Fig. 6.

5) For BBB ---- structure a resonance form shown in Fig. 6 can be considered. This means that in some case the polypeptide chain may form an extended oscillator just as a molecular chain with conjugated double bond and thus we may explain by a field of forces resulting from this oscillator the mechanism of the combination of dyes with proteins, etc.

III. The Structure of α-keratin. No satisfactory explanation for the structure of α-keratin has hitherto been advanced. However, we consider that BBB ---- or BBEBBE ---- can represent this structure by which we can explain reasonably the experimental data obtained for α-keratin as follows:

1) The period along the fiber axis observed for α-keratin amounts to 5.15 A, which is in good agreement with that predicted from the structure BBB -----. The side chain spacing is found to be 9.8 A in β-keratin as well as in α-keratin. This is comprehensible, if we consider that cystine bond remains unchanged in both keratins (see Fig. 7 and 8).

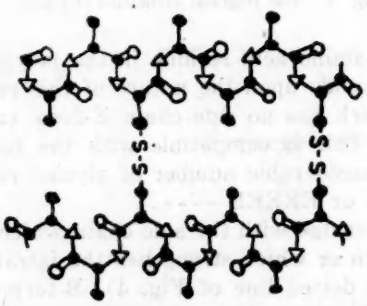

Fig. 7. Cystine bond in α-keratin.

The backbone spacing 4.65 A of β-keratin is not found in α-keratin. This will be due to the disconnection of intermolecular hydrogen bond of β-keratin which in turn forms the intramolecular hydrogen bond of

α-keratin denoted by the dotted lines of Fig. 4.

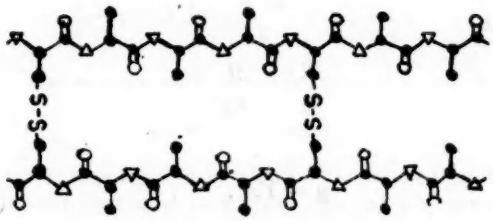

Fig. 8. Cystine bond in β-keratin.

The supercontraction of wool may also be explained, if, for example, we consider a structure such as shown in Fig. 9, which can be obtained by the disconnection of cystine chain.

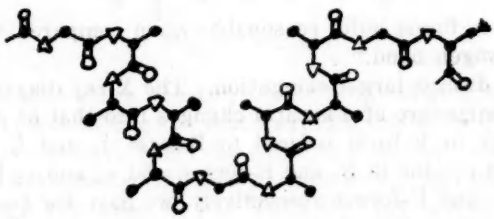

Fig. 9. An example of the structure of supercontracted wool.

2) Let us next discuss the mechanical properties of wool. For an elongation Δl within 2% Hooke's law is found to hold. We have, therefore,

$$E = \frac{1}{2}k(\Delta l)^2 \qquad (1)$$

where E is the change in energy and k the force constant. Let y be Young's modulus refered to a single molecule and l_0 be an equilibrium length of an amino acid residue along the chain. Then y is defined as:

$$y = \frac{\partial E}{\partial \Delta l} \Big/ \frac{\Delta l}{l_0} \qquad (2)$$

From Eq. (1) and (2) we have

$$y = kl_0 \qquad (3)$$

The value of Young's modulus Y in its ordinary sense can be obtained from the experimental relation[7] between the tension K and the elongation $\Delta L/L_0$:

(7) Astbury and Coworkers: *Phil. Trans. Roy. Soc.* (London), A 230 (1931), 75; 232 (1933), 333; *Trans. Farad. Soc.*, 29 (1933), 193; *Proc. Roy. Soc.* (London), A 150 (1935), 533.

$$Y = K\Big/\frac{\Delta L}{L_0} = \frac{10 \times 10^5}{0.02} = 5 \times 10^7 \text{ g/cm}^2 \qquad (4)$$

We can now put

$$\frac{\Delta l}{l_0} = \frac{\Delta L}{L_0}$$

$$y = YA\,,$$

where A denotes the molecular cross section. This can be calculated from the observed side chain spacing 9.8 A of α-keratin and the backbone spacing which is assumed reasonably to be 6 A. We have then

$$k = \frac{y}{l_0} = \frac{YA}{l_0} = \frac{(5 \times 10^7 \times 980)(9.8 \times 6 \times 10^{-16})}{2.57 \times 10^{-8}} = 1.1 \times 10^4 \text{ dyne/cm} \qquad (5)$$

This value of k is found quite reasonable when compared with the force constant of hydrogen bond.[8]

Let us next discuss larger elongation. The X-ray diagram shows that in this case the structure of α-keratin changes into that of β-keratin. Let E_2 be the energy of E-form refered to B-form, l_1 and l_2 be the length of an amino acid residue in B- and E-forms, and n_1 and n_2 be the number of residues in B- and E-forms, respectively, we have for the length L and energy E of a polypeptide chain

$$L = n_1 l_1 + n_2 l_2 = n l_1 + n_2 (l_2 - l_1) \qquad (6)$$

$$E = n_2 E_2 \qquad (7)$$

where $$n = n_1 + n_2$$

In the case of the coexistence of both forms the tension per unit chain K is calculated as

$$KA = \frac{\partial E}{\partial L} = \frac{\partial E}{\partial n_2}\frac{\partial n_2}{\partial L} = \frac{E_2}{l_2 - l_1} \qquad (8)$$

From this relation we see that all B-forms change into E-forms for a certain value of tension, at which the tension-elongation curve becomes parallel to the elongation axis. That such is not actually the case is due to the neglection of entropy in the foregoing discussion. The value of entropy will be very small in both extreme cases where all amino acid residues take B- or E-form, but in the intermediate case its value will be considerable, so that the said curve inclines to the elongation axis to some extent. If we put the value of tension 6×10^5 g/cm^2 (corresponding to the middle point of the slope of tension-elongation curve observed in

(8) Halford: *J. Chem. Phys.*, 14 (1946), 395.

the measurement for the relative humidity of 100%) into K of Eq. (8) and put

$$l_2 - l_1 = 3.32 - \frac{5.14}{2} = 0.75\,\text{A}\,,$$

we can calculate the energy difference between B- and E-forms as:

$$E_2 = 370\ \text{cal/mol}$$

The structure of α-keratin may also be considered as BBEBBE ....[9] (see Fig. 10), for which the period along the main chain is calculated as 10.3 A. This is also compatible with the experiment.[10]

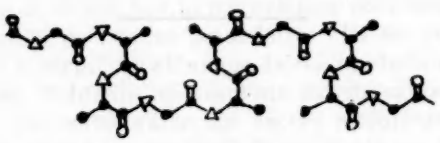

Fig. 10. α-keratin.

In this case the side chain (cystine bond) is directed upwards or downwards from the plane of Fig. 10, and therefore, the corresponding spacing (9.8 A) remains constant, when the chain is stretched out. If, therefore, we assume the backbone spacing as 9 A, we can calculate the force constant k and the energy difference E_2 just as in Eq. (5) and (8):

$$k = \frac{(5\times10^7\times980)(9.8\times9\times10^{-16})}{5.15\times10^{-8}} = 0.84\times10^4\ \text{dyne/cm},$$

$$E_2 = KA(l_2 - l_1) = 1800\ \text{cal/mol (residue)}.$$

The elongation of wool will not be explained by a single mechanism, as the experiment of Bull[11] shows. (The electron microscope experiment[12] shows that keratin fiber has specific fine structure, and, therefore, it may consist of complex micelles.). Hence the foregoing discussion will not cover all the elongation steps. However, since X-ray diagram shows the structural change (α to β change) after elongation, it will be difficult to explain the mechanical property of keratin fiber without taking into account the intramolecular rotation as stated above.

(9) This can be considered as a structure in the state of supercontraction, if the structure of keratin fiber in its ordinary state is represented by the configuration shown in Fig. 4.

(10) The intensity relation of X-ray scattering may more reasonably be explained by the structure of Fig. 10 than that shown in Fig. 4. We are indebted to Dr. N. Tanaka for the discussion on this structure.

(11) Bull: *J. Am. Chem. Soc.*, **66** (1944), 1253; **67** (1945), 533.

(12) Mercer: *Nature*, **159** (1947), 535. See also Bear: *J. Am. Chem. Soc.*, **65** (1943) 1784; **66** (1944), 2043.

The discussion of globular proteins based on the structure proposed by us will be given in a later communication.

Faculty of Science and Radiation Chemistry
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Études spectrochimiques des complexes métalliques renfermant la molécule triazène. I[1]. Sur les triazènes dinitrés.

Par Taku UÉMURA, Yasuhisa SATO et Shun-ichi ARIKAWA.

(Reçu le 6 juillet 1948.)

Introduction. Plusieurs auteurs, comme R. Meldola,[2] O. Dimroth,[3] F. M. Perkin[4] et A. Mangini,[5] ont déjà observé les sels métalliques des amines secondaires et ils ont fait la méthylation pour savoir quel azote du triazène a la fonction de l'amine secondaire. Ils les ont décomposés et ont essayé de tirer la structure chimique de ces produits décomposés, mais ils n'ont pas réussi d'obtenir les résultats satisfaisants. W. Watt[6] et F. P. Dwyer[7] et son collaborator ont encore minutieusement étudié les mêmes matières et surtout Dwyer publiait une étude sur la constitution de "chelation" d'anneau des quatre membres. Les présents auteurs ont mesuré les spectres d'absorption de triazène et ses dérivés métalliques pour éclairer la struture chimique et le caractère salifiable par leurs études spectroscopiques. Ils ont d'abord pris le triazène (C_6H_5-N=N-NH-C_6H_5, benzène-diazo-aminobenzène ou diazoamidobenzol), corps fondamantal, et ses dérivés dinitrés pour en rendre compte dans le présent mémoire. Ils ont encore l'intention de continuer leurs recherches sur les sels complexes métalliques conduits des composés ci-dessous indiqués.

Synthèse des échantillons. Les échantillons que nous avons employés pour nos études ont été tous préparés par les méthodes déjà connues. Nous avons utilisé le dinitro-triazène que nous avons obtenu avec la nitraniline purifiée par les recristallisations répétées d'alcool et d'eau chaude. Le point de fusion de ces nitranilines que nous avons employées se présentent respectivement 147° pour le para-composé, 72° pour l'ortho- et 112° pour le méta-. Le dinitro-triazène synthétisé a été encore purifié par plusieurs recristallisations de l'alcool (Table 1). Les corps obtenus sont généralement des cristallines fines et celles de 3,3'-dinitro-triazène étaient comme une masse de coton constituée par de petits cristaux aiguillés.

(1) Exposé fait lors de la 68e Séance annuelle de la Société chimique du Japon, octobre 1946.

(2) R. Meldola et F. W. Streatfeild, *J. Chem. Soc.*, **49** (1886), 624; **50** (1887), 102, 434; **51** (1888), 664.

(3) O. Dimroth, *Ber.*, **40** (1907), 2390.

(4) F.M. Perkin, *Ber.*, **30** (1897), 1394.

(5) A. Mangini, *J. Soc. Chem. Ind.*, **58** (1939), 327.

(6) W. Watt, *Z. anorg. allgem. Chem.*, **221** (1935), 187.

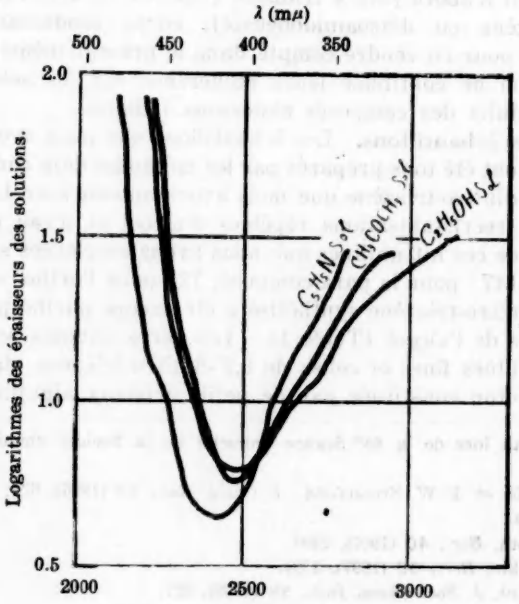
(7) F.P. Dwyer, *J. Soc. Chem. Ind.*, **56** (1937), 70; **57** (1938), 351, 357; **58** (1939), 110; *J. Am. Chem. Soc.*, **63** (1941), 78; F. P. Dwyer et D.P. Mellor, *J. Am. Chem. Soc.*, **63** (1941), 81.

Table 1.

Dinitro-triazène	4,4′—	2,2′—	3,3′—	4,2′—	2,4′—	4,3′—	3,4′—	2,3′—	3,2′—
Point de fusion (C°) (Décomposition)	221°	198°	194°	193°	192°	222°	223°	171°	170°
Couleur	jaune	jaune	jaunâtre	jaune orangé	jaune orangé	jaune	jaune	jaune	jaune

F. P. Dwyer[7] a observé qu'il y a deux types (jaune et orangé ou rouge violet) dans les dinitro-triazènes, excepté le 3,3′-composé, et il a réussi à séparer les deux types de 4,4′- et 2,2′ composés aux quels il a donné les noms: "type normal" à modification jaune, "type aci" à modification rouge. D'autre part, A. Mangini[5] a attribué ces deux modes aux isoméries géométriques cis- et trans-. Nous avons seulement pris les échantillons synthétisés recristallisés de l'alcool pour photographier les spectres et nous n'avons essayé aucune séparation du composé que Dwyer a nommé "original". Nous croyons que ces deux modifications contiennent en quantité équivalente dans nos corps préparés et nos études spectrochimiques nous ont confirmé notre supposition, c'est-à-dire, nous n'avons pas pu trouver l'absorption caractéristique de ces deux types.

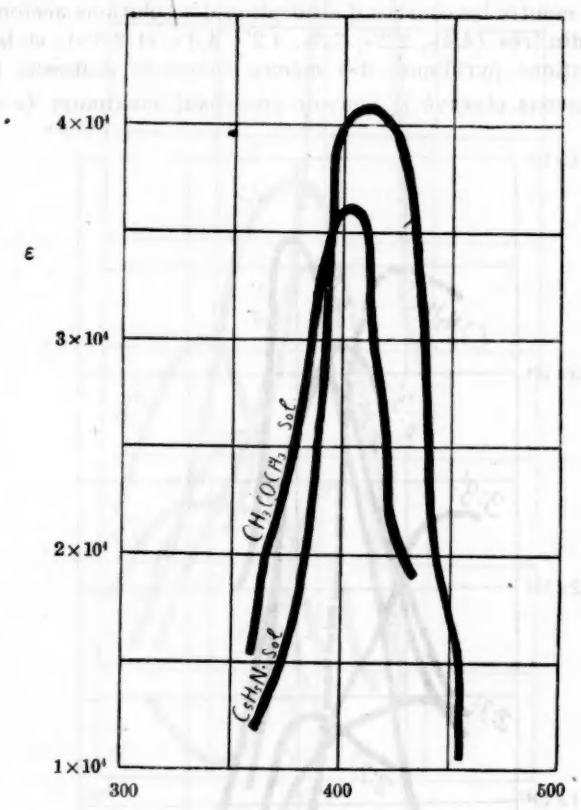
Influences des dissolvants. Le triazène et le dinitro-triazène sont peu solubles dans l'eau et le benzène, bien solubles dans le phénol, l'acétone et



4,4′-Dinitro-triazène.

Fig. 1.

la pyridine. La Fig. 1 expose qualitativement les spectres d'absorption du 4,4'-dinitro-triazène dissous dans l'alcool, l'acétone et la pyridine. La solution alcoolique et celle d'acétone donnent à peu près le même résultat tandis que la solution pyridique montre une courbe un peu différente. On a quantitativement mesuré en employant l'acétone et la pyridine comme ses dissolvants (Fig. 2).



4,4'-Dinitro-triazène.

Fig. 2.

La solution pyridique nous a donné ses spectres d'absorption bathochromiques ayant un grand pouvoir absorbant, et l'acétone qui a l'absorption semblable à celle de l'alcool, était choisie comme échantillon, car la première est plus soluble que le second. La pyridine et l'acétone ont leurs absorptions dans la région des longueurs d'onde plus courtes que 330 mμ. Comme leur principale bande d'absorption se trouve cependant dans la

région visible ou son voisinage ultraviolet, ces deux dissolvants peuvent être adopter.

Relation entre la position du radical nitré et l'absorption du rayon lumineux. Les spectres d'absorption du diazoamidobenzol (triazène) ont été comparés avec ceux de ce composé dinitré pour savoir les effets de la position du radical nitré.

La Fig. 3 montre les courbes d'absorption des solutions acétoniques de six triazènes dinitrés (4,4′-, 2,2′-, 3,3′-, 4,2′-, 4,3′-, et 2,3′-), et la Fig. 4, celles des solutions pyridiques des mêmes composés ci-dessus nommés.

Nous en avons observé le pouvoir absorbant maximum (ε max) et

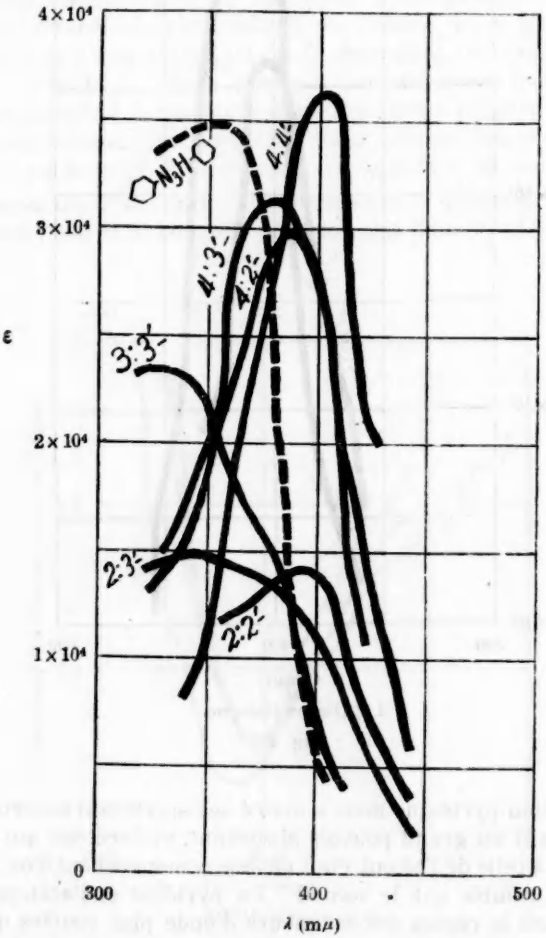


Fig. 3. Triazène et dinitro-triazènes (solutions acétoniques).

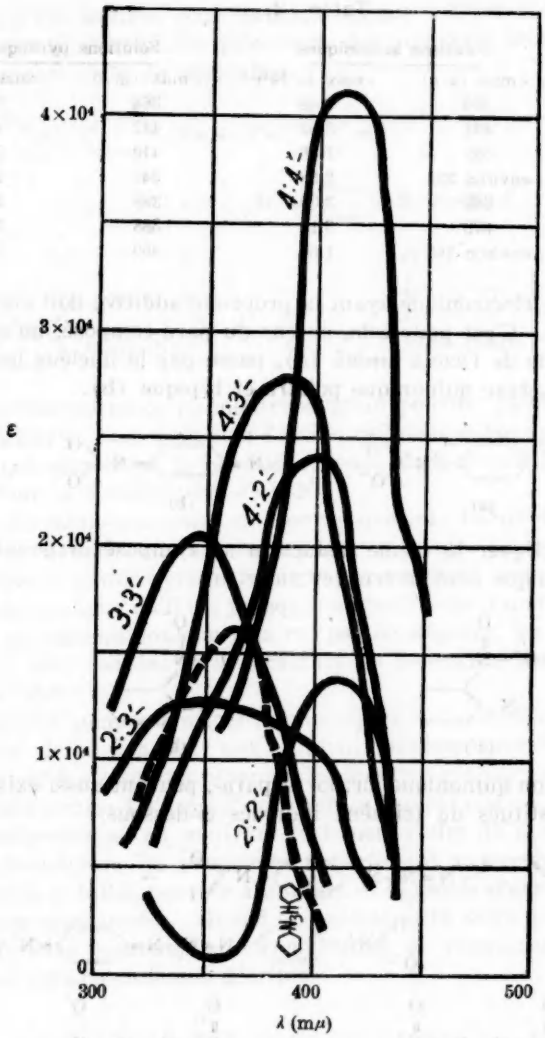


Fig. 4. Triazène et dinitro-triazènes (solutions pyridiques).

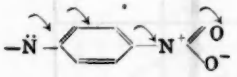
la longueur d'onde maximum correspondante (λ max) que nous avons donnés dans la Table 2.

Quand le radical nitré entre la para-position ou l'ortho-position envers le radical diazoaminé, la bande d'absorption change vers des longueurs d'onde plus élevées. Ces effets bathochromiques ont probablement apparu par la transformation du type benzénique en celui de quinone (quinonique). Le radical nitré renferme généralement la liaison de son π-type, et comme la structure de résonance comparablement stable est toujours possible

Table 2.

	Solutions acétoniques		Solutions pyridiques	
	λ max. (mμ)	ε max. (×10⁴)	λ max. (mμ)	ε max. (×10⁴)
Triazène	350	3.48	364	1.60
4,4′-dinito-triazène	401	3.62	412	4.09
2,2′-dinitro-	397	1.46	410	1.38
3,3′-dinitro-	environ 330	2.38	347	2.03
4,2′-dinitro-	386	3.00	398	2.42
4,3′-dinitro-	378	3.15	388	2.78
2,3′-dinitro-	environ 345	1.50	350	1.28

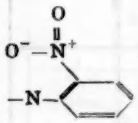
d'exister, la paire électronique ayant la propriété additive doit être donnée à l'atome d'azote. C'est pour cela, au cas du para-composé, qu'une paire électronique partie de l'azote aminé (a), passe par le nucléus benzénique et produit la structure quinonique polaire et typique (b).



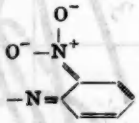
(a)

(b)

On peut appliquer la même déduction au composé ortho-nitré et le type ortho-quinonique peut se trouver (a′ et b′).

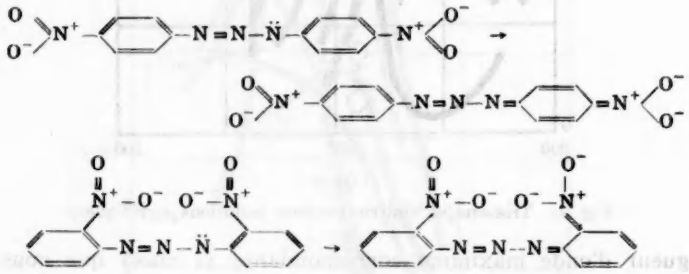


(a′)



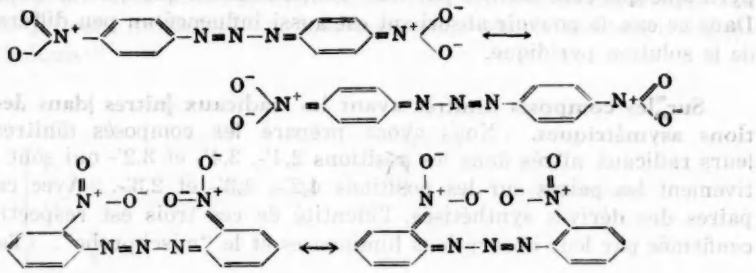
(b′)

La constitution quinonique, ortho- et para-, peuvent aussi exister dans les produits substitués du triazène indiqués ci-dessous.



Cette transformation explique que les doubles liaisons conjuguées se produisent entre les deux radicaux nitrés dans les composés, ortho- et para-, en montrant la constitution polaire. On peut trouver en même temps que le para-composé prend plus facilement la structure symétrique que l'ortho-. Le moment bipolaire du para-composé peut aussi bien augmenter que celui du ortho- et sa variation est naturellement grande et

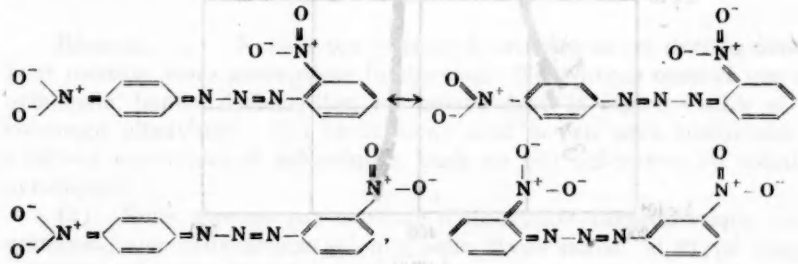
son absorption devient plus bathochromique. C'est encore possible de supposer que la constitution quinonique des composés, ortho- et para-, peut prendre encore celle de résonance.



Les ortho-composés ne montrent qu'un pouvoir absorbant considérablement faible et c'est peut-être l'action mutuelle entre les radicaux nitré et aminé qui empêchent la résonance, mais, dans ce cas, il serait possible de constituer la combinaison -O-H-N-.

Pour les méta-composés, on observe que leur bande d'absorption a la tendence de devenir un peu vague, leur pouvoir absorbant n'est pas remarquable et plutôt hypsochromique le comparant avec le triazène non-nitré. Cela explique qu'il est presque impossible de transformer ces méta-composés au type quinonique polaire; par conséquent, les doubles liaisons conjuguées sont coupées et la structure de résonance stable ne peut pas être manifestée.

Quant aux composés nitrés asymétriques, on peut déduire de pareilles conclusions déjà données aux dinitro-triazènes symétriques, et les confirmer par les résultats obtenus des spectres d'absorption, c'est-à-dire, les composés comme 4,2'- et 4,3'- qui ont un radical nitré à la para-position, sont bathochromiques en montrant fortement l'effet du radical, tandis que, dans le 2,3'-composé, les propriétés appartenant aux ortho- et méta-composés, comme le faible pouvoir absorbant et la bande d'absorption diffusée, peuvent être superposées. Quand un radical nitré entre à la méta-position dans un nucléus benzénique, la constitution de résonance stable n'existe pas par les raisons ci-dessus décrites.



La bande d'absorption de la solution pyridique est plus faible que

cellé donnée par la solution acétonique, mais cette absorption manifeste l'effet bathochromique assez fort, c'est-à-dire, le triazène et ses dérivés 3,3′- et 2,3′-dinitrés donnent une bande d'absorption plus claire en solution pyridique que celle donnée par leur solution acétonique qui est assez large. Dans ce cas, le pouvoir absorbant est aussi influencé un peu différemment de la solution pyridique.

Sur les composés dinitrés ayant les radicaux nitrés dans les positions asymétriques. Nous avons préparé les composés dinitrés ayant leurs radicaux nitrés dans les positions 2,4′-, 3,4′- et 3,2′- qui sont respectivement les paires sur les positions 4,2′-, 4,3′- et 2,3′-. Avec ces trois paires des dérivés synthétisés, l'identité de ces trois est respectivement confirmée par leur absorptions lumineuses et le "mischprobe". (Table 3.)

Table 3.

Radicaux nitrés	4,2′—	2,4′—	4,3′—	3,4′—	2,3′—	3,2′—
Point de fusion	193°	192°	222°	223°	171°	170°
"mischprobe"		191°		221°		170°

On comprendra cette confirmation par la courbe d'absorption de

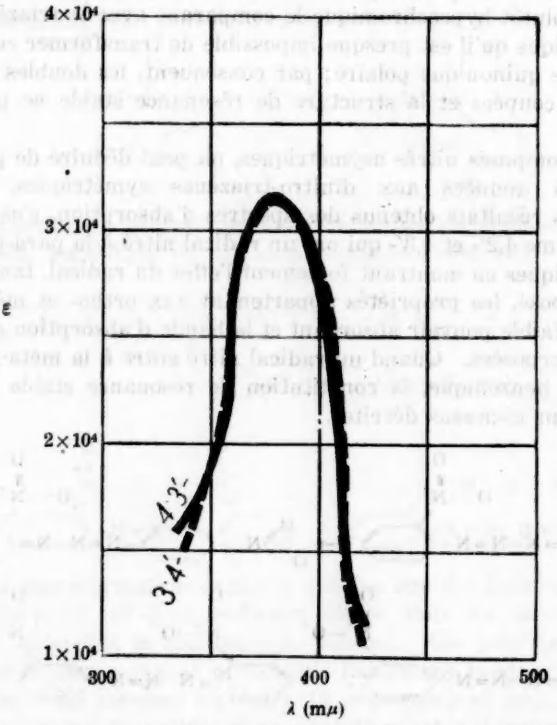
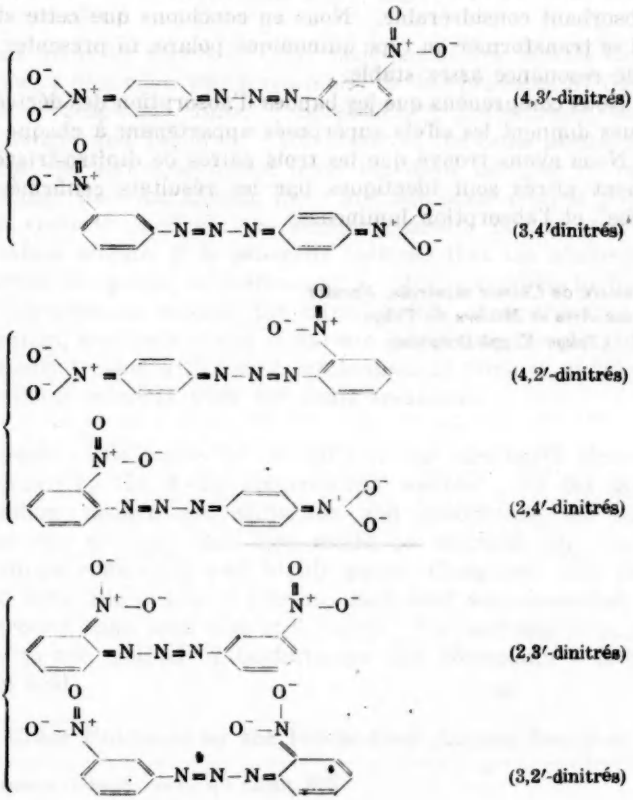


Fig. 5. 4,3′- et 3,4′-Dinitro-triazènes (solutions acétoniques).

l'exemple de Fig. 5 où l'on a pris les deux triazènes 4,3′- et 3,4′-dinitrés dissous dans l'acétone.

Ces expériences nous montrent que les radicaux nitrés asymétriquement entrés des trois paires donnent essentiellement peu de différences aux résultats qui nous présentent une base forte pour déterminer leur constitution chimique.[8]



Résumé. (1) Nous avons préparé le triazène et ses dérivés dinitrés pour mesurer leurs absorptions lumineuses. Nous avons observé que leur principale bande d'absorption se trouve dans la région visible et son voisinage ultraviolet. Ces absorptions sont à peu prés semblables en solutions alcooliques et acétoniques, mais un peu différentes en solutions pyridiques.

(2) Nous n'avons pas constaté d'absorption caractéristique correspondante aux deux modes qu'on appelle "type jaune" et "type rouge".

(8) Meldola a prouvé l'identité des isomères par ses produits de la décomposition[2].

(3) Nous avons désigné au para- composé la structure quinonique stable et polaire qui peut montrer un pouvoir absorbant fort et bathochromique et la résonance.

(4) Nous pouvons supposer que le petit pouvoir absorbant du l'ortho-composé est probablement dû à une action mutuelle entre les radicaux nitré et aminé en affaiblissant la résonance.

(5) Le méta-composé ne manifeste ni effet bathochromique, ni pouvoir absorbant considérable. Nous en concluons que cette structure ne peut ni se transformer en type quinonique polare, ni présenter de constitution de résonance assez stable.

(6) Nous comprenons que les bandes d'absorption des dérivés nitrés asymétriques donnent les effets superposés appartenant à chaque radical.

(7) Nous avons trouvé que les trois paires de dinitro-triazène asymétriquement nitrés sont identiques par les résultats confirmés par le "mischprobe" et l'absorption lumineuse.

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On the Color Reaction Between Iodine and the Basic Acetates of Some Rare Earth Elements.

By Kenjiro KIMURA and Nagao IKEDA.

(Received July 6, 1948.)

It was found by Damour[1] that basic lanthanum acetate acting with iodine shows a blue color which resembles to that produced by the familiar iodine-starch reaction. Biltz,[2] Berczeller,[3] Lottermoser and Herrmann,[4] Krüger and Tschirch,[5] etc. observed the same phenomenon.

As for the action of iodine upon the basic acetates of rare earth elements other than lanthanum, there are also some reports published.[6] Although Orlow[7] noticed the similar reaction in the case of basic praseodymium acetate, it is generally believed that the above-mentioned color reaction is specific to lanthanum.[8] But, according to the present authors' experiments, besides the basic acetate of lanthanum, those of praseodymium, neodymium and samarium take on an intense indigo color when properly treated with iodine, while those of yttrium, gadolinium and erbium remain colorless with the same treatment.

Materials. The purity of the salts of the rare earth elements used was examined by the X-ray spectroscopic method. As for lanthanum, praseodymium, neodymium, samarium and gadolinium, the amount of impurities was so small that they might be assumed for the present purposes to be sufficiently and highly pure. Compared with the above-mentioned salts, the purity of yttrium salts used was somewhat low, and that of erbium salts used was still lower. The acetates were prepared according to the method of Lottermoser and Herrmann[9] from oxides and acetic acid.

The Color Produced by the Iodine-Basic Acetate Reaction. A solu-

(1) Damour, *Compt. rend.*, 43 (1856), 976.

(2) Biltz, *Ber.*, 37 (1904), 719.

(3) Berczeller, *Biochem. Zt.*, 84 (1917), 160.

(4) Lottermoser, *Kolloid-Zt.*, 33 (1923), 271; Lottermoser u. Herrmann, *Z. physik. Chem.*, 122 (1926), 1.

(5) Krüger u. Tschirch, *Ber.*, 62 (1929), 2776; 63 (1930), 826.

(6) e.g. Damour, *op. cit.*; Behrens, *Chem. CB.*, (1902) I, 296; Orlow, *Chem-Ztg.*, 31 (1907), 45; Krüger u. Tschirch, *op. cit.*

(7) Orlow, *op. cit.*

(8) Krüger and Tschirch (*op. cit.*) described in their first report that basic praseodymium acetate showed the color reaction with iodine, but later they considered that it was due to the impureness of the materials used and, in their second report, withdrew what was stated in their former report.

(9) *op. cit.*

tion of each acetate was treated with ammonia[10] and basic acetate was precipitated. A solution of iodine and potassium iodide was added to it. Being left at room temperature for 2 or 3 days, it took on gradually a color[11] mentioned in the second column of Table 1. But when it was heated about 10 minutes by immersing the vessel in the boiling water, an indigo color developed immediately in the cases of lanthanum, praseodymium, neodymium and samarium as shown in the third column of Table 1. For comparison, the descriptions of Krüger and Tschirch,[12] which are quite different from ours in the cases of praseodymium, neodymium and samanium, are given in the fourth column of Table 1.

Table 1. The Colors of Iodine-Basic Acetates.

Elements	When left at room temperature	When heated in the boiling water	According to Krüger and Tschirch
Yttrium	Colorless	Colorless	Colorless
Lanthanum	Indigo	Indigo	Indigo
Praseodymium	Blue	Indigo	Colorless
Neodymium	Bluish violet	Indigo	Colorless
Samarium	Yellow	Indigo	Colorless
Gadolinium	Colorless	Colorless	—
Erbium	Colorless	Colorless	Colorless

The colored precipitate, after being left 2 days at room temperature and after the removal of free iodine from it, was shaken vigorously with

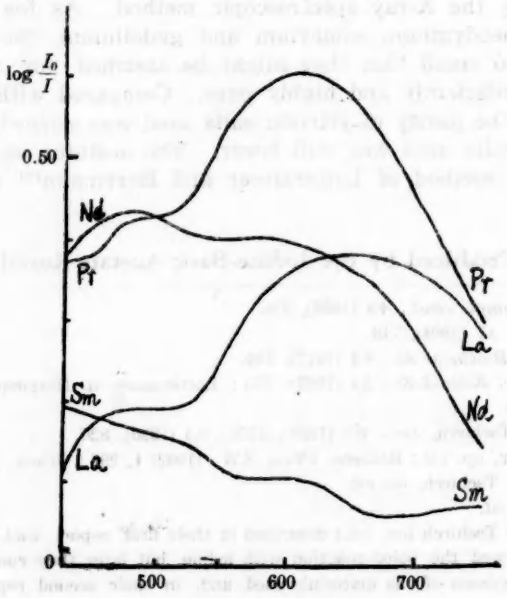

Fig. 1.

water. The water took on the same color as the precipitate. The colored solution thus formed was separated from the precipitate with the aid of a centrifuge and was examined with the Pulfrich photometer. The absorption curves obtained are given in Fig. 1, where I_0 denotes the intensity of the initial light and I, that of the light transmitted.

It is seen from the figure that the absorption maximum of lanthanum salt lies in the longest wave-length side, and those of the salts of the other elements shift to the shorter wave-length side in the order of praseodymium, neodymium and samarium. The absorption maximum of samarium salt does not appear in the visible part.

From this fact, it may be allowed to conclude that the absorption maximum of the iodine-basic acetate color shifts to the shorter wave-length side with the increase of the atomic numbers of the rare earth elements, i.e. with the decrease of the basicity of the elements. The colorlessness of the iodine-basic acetates of gadolinium, erbium and yttrium, which was shown in the experiments, may also be expected from this rule.

The Change of Color with the Lapse of Time. As Berczeller[13] and Lottermoser[14] already pointed out, the color of iodine-basic lanthanum acetate changes from reddish brown or brown to blue with the lapse of time. We studied the color change with the Pulfrich photometer. The experimental procedure was as follows.

To 1 ml. of lanthanum acetate solution[15] were added 0.3 ml. of 1N. ammonia and 2 ml. of 0.1N. iodine-potassium iodide solution. The mixture after being left at room temperature for a definite time mentioned in Fig. 2, was treated in the same way as already mentioned; thus the solution for the photometric measurement was prepared. The absorption curves obtained are given in Fig. 2.

From this figure, it would be seen that the absorption maximum shifts to the longer wave-length side with the lapse of time,[17] and that

(10) The color did not appear when a large excess of ammonia was used; so such large excess of it should be avoided. Also the insufficient quantity of it should be avoided, as such insufficient quantity caused the incomplete precipitation of basic acetate.

(11) In order to remove the yellow or brown color due to free iodine, the precipitate after the treatment was washed with water by decantation with the aid of a centrifuge. Then the color was observed.

(12) In stead of acetates, Krüger and Tschirch (*op. cit.*) used the mixture of the nitrates of the rare earth elements and sodium acetate. We also carried out the experiments with the same mixtures as theirs but, contrary to their results, we confirmed that praseodymium, neodymium and samarium showed the above mentioned color reaction.

(13) *op. cit.*

(14) *op. cit.*

(15) 1 ml. of the solution corresponds to 11.5 mg. of La_2O_3.

(16) The room temperature was between 10.4°C and 16.4°C during these experiments. Any particular attentions to keep the temperature constant were not paid.

(17) Immediately after the addition of iodine solution, the basic lanthanum acetate takes on a reddish brown color. After 1 hour, it becomes reddish violet, after 5 hours, violescent indigo and finally it takes on an indigo color.

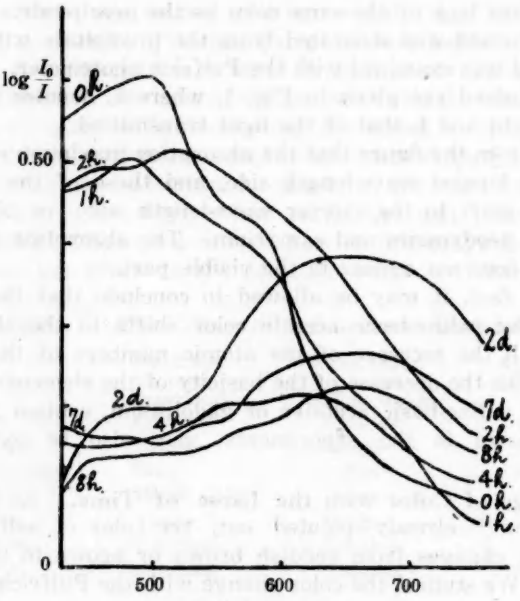

Fig. 2.

the shape of the curve after 8 hours is similar to that after 7 days, in other words, the final indigo color appears already in 8 hours and is stable at least for 7 days.

The similar results were obtained with praseodymium and neodymium, but compared with lanthanum, the color changes somewhat more slowly with these elements.

The Relation between the Concentration of Iodine and the Quantity of Sorbed Iodine. As for the relation between the concentration of iodine and the quantity of sorbed iodine, Lottermoser[18] pointed out that Freundlich's sorption isotherm holds good in the case of basic lanthanum acetate. According to our experiments, it also holds good in the cases of the basic acetates of praseodymium and neodymium.

The Mechanism of the Interference of Other Ions. As for the effect of other ions upon the color of iodine-basic lanthanum acetate, many experimental results were reported by Krüger and others.[19] According to them, the presence of other rare earth elements greatly interfered with the formation of the blue colored substance, but it is not so in our experiments with praseodyminum and neodymium. The mixture of the basic acetates of lanthnum, praseodymium and neodymium also took on an indigo color and no mutual interference was recognized. But the interfering effect of the rare earth elements which did not show the

(18) *op. cit.* (19) *op. cit.*

above-mentioned color reaction was considerable. For example, when yttrium was present in a quantity larger than 0.7:1 in the atomic ratio to lanthanum, no coloration of basic lanthanum acetate was seen.

It is also mentioned in the literature that the interfering effect of fluoride ions, sulfate ions, etc. is remarkable, while that of nitrate ions, chloride ions, etc. is not much. But no satisfactory explanation of the mechanism of the effect of these ions is hitherto given. One possible explanation by the present authors is as follows. When a lanthanum solution containing acetate ions and the interfering ions, e.g. sulfate ions, is treated with ammonia, the basic lanthanum sulfate, which shows no color reaction with iodine, precipitates in earlier stages and interferes with the action of the basic lanthanum acetate which precipitates later. On the contrary, when a lanthanum solution containing acetate ions and the non-interfering ions, e. g. nitrate ions, is treated with ammonia, the precipitation of the basic lanthanum acetate occurs before that of the basic lanthanum nitrate which shows no color reaction with iodine, and the action of basic lanthanum acetate is not greatly interfered. The results of the following experiments seem to support such an interpretation.

(1) A solution containing lanthanum acetate and ammonium sulfate was treated with an insufficient amount of ammonia. The precipitate thus formed showed no color reaction even when it was heated. But the precipitate formed with a sufficient quantity of ammonia took on an indigo color with iodine.

(2) When a solution containing a larger amount of sulfate ions was treated with a sufficient quantity of ammonia, the precipitate thus formed took on only a faint color with iodine. But, even in such a case, if a solution, after the previous removal of the precipitate which was formed with an insufficient amount of ammonia, was treated again with ammonia, the precipitate then formed showed distinctly the color reaction.

(3) When the amount of sulfate was still larger and exceeded the quantity equivalent to lanthanum, no colored precipitate was produced in spite of the presence of acetate ions in the solution. In such a case, the previous removal of the precipitate formed in earlier stages just mentioned above was of no use.

(4) The precipitate, which was formed with a small amount of ammonia from a solution containing lanthanum acetate and lanthanum nitrate, took on an indigo color with iodine. But the precipitate formed with a larger amount of ammonia was only unevenly colored with dirty violescent indigo. When the solution was treated with ammonia after the previous removal of the precipitate, which was produced with an insufficient amount of ammonia and showed the color reaction, the precipitate thus formed remained almost colorless with iodine.

(5) As already mentioned above, the basic acetate precipitate which was formed from a solution containing lanthanum acetate and a considerable quantity of yttrium acetate, did not show the color reaction with iodine. But when the method of fractional precipitation with ammonia

was applied to such a solution, the precipitate in earlier stages did not show the color reaction, while that in later stages took on an indigo color with iodine. This showed that the precipitation of basic yttrium acetate occurred before that of basic lanthanum acetate.

The above-mentioned experimental results seem to support our interpretation on the mechanism of the effect of some anions and cations. Hitherto little attention was paid by earlier authors to the quantity of ammonia used, but it is obvious from the above-mentioned experiments that the amount of ammonia added to form basic acetate precipitate plays always an important role.

Summary. (1) The color reaction between iodine and basic acetate is not, as is often believed, peculiar to lanthanum. It is shown also by praseodymium, neodymium and samarium.

(2) The absorption maximum of iodine-basic acetate shifts to shorter wave-length side with the decrease of the basicity of the rare earth elements.

(3) The color change of iodine-basic acetate with the lapse of time was studied photometrically.

(4) It was confirmed that the sorption isotherm holds good in the cases of the basic acetates of lanthanum, praseodymium and neodymium.

(5) The effect of other ions on the color reaction was discussed.

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Tokyo University.

CORRECTIONS.

Volume 19, 1944. (No. 12.)

Page

213 Omit the 12th. line-(Reçu le 28 octobre 1944.), add the same just below the 2nd. line-Par Kazuo KURODA.

215 To the 'Page'-column of 21th. line add 213.
To the 'Page'-column of 13th. line from the bottom add 185.
To the 'Page'-column of 4th. line from the bottom add 207.

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